Variational Monte Carlo:

$$H\psi = E\psi \qquad \psi(\vec{R}) \qquad \vec{R} = (\vec{r}_1, \vec{r}_2, \cdots \vec{r}_N)$$

Only interested in E_0 + ψ_0 ground state

$$E_V = \frac{\int \psi^* H \psi \, d\vec{R}}{\int |\psi|^2 d\vec{R}} > E_0$$

$$= \frac{\int (H\psi)/\psi \, (\psi\psi^*) \, d\vec{R}}{\int |\psi|^2 d\vec{R}}$$

$$\boxed{E_L(r) = \frac{H\psi}{\psi}}$$

local energy

$$= \int E_L(\vec{R}) \, P(\vec{R}) \, d\vec{R} \qquad \vdots P(\vec{R})$$

if $\psi \to \psi_0$

$E_L(r) \to E_0$

const.

$$P(\vec{R}) = \frac{|\psi(\vec{R})|^2}{\int |\psi|^2 d\vec{R}}$$

$$E_V = \langle E_L \rangle = \frac{1}{n} \sum_{i=1}^{n} E_L(\vec{R}_i)$$

$$\text{with } \underbrace{\vec{R}_i \in P(\vec{R})}_{\text{By the Metropolis algorithm}}$$

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How to choose ψ? the trial ground state

$V(r) = -\frac{Z}{r}$ $\quad V_{LJ}(r) = \epsilon_0\left(\frac{1}{r^{12}} - \frac{1}{r^6}\right)$ etc.

↳ short-range, hard-core potential

$\rightarrow -\frac{1}{2\mu}\nabla^2\psi + V(r)\psi = E\psi$

μ = reduced mass

dimensionless form : $-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E$

choose r_0 basic unit of length.

$r = r^* r_0$

$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi \dots$

$-\frac{\hbar^2}{2m}\frac{1}{r_0^2}\left(\frac{\partial^2}{\partial x^{*2}} + \dots\right)\psi \dots = E\psi$

$E_0 = \frac{\hbar^2}{m}\frac{1}{r_0^2}$ $\qquad + V\psi = E\psi$

$-\frac{1}{2}\cancel{E_0}\nabla_*^2\psi + \frac{V}{E_0}\psi = E^*\cancel{E_0}\psi$

$\underbrace{V = V^* E_0}$

$$\boxed{-\frac{1}{2}\nabla_*^2\psi + V^*\psi = E^*\psi}$$

choose r_0 such that V^* is the simplest!

4 $V^* = -\frac{Z}{r}$ if r_0, E_0 are the atomic units.

$E_0 = -\frac{1}{2}\frac{1}{n^2}$ Hartree

$= -\frac{1}{n_x} R_b$ $\qquad$ Hartree $= 2R_b$.

$$-\frac{1}{2\mu}\nabla^2\psi + V(\overset{\psi}{\psi}) = E\psi$$ for the g.s. $\psi > 0$

$$\psi = e^{-S(r)} \qquad \vec{\nabla}\psi = -\vec{\nabla}S\, e^{-S(r)}$$

$$-\frac{1}{2\mu}\left[-S''(r) - \frac{2}{r}S' + (S')^2\right]\cancel{\psi} + V(r)\cancel{\psi} = E\cancel{\psi}$$

$$\vec{\nabla}^2\psi = \left[-\nabla^2 S + (\nabla S)^2\right]\psi$$

$$= \left[-\frac{\partial^2}{\partial r}S - \frac{2}{r}S' \qquad \overset{\shortparallel}{\left(\frac{\partial S}{\partial r}\right)^2} \qquad \vec{\nabla}S = S'\hat{r}$$

$$E_L = \frac{1}{2\mu}S'' + \frac{1}{\mu}\frac{S'}{r} - \frac{1}{2\mu}(S')^2 + V(r) = E$$ Riccati-Eq.

must cancel the singularity in V(r)

$\downarrow$ $-\frac{Z}{r}$ or $\epsilon\left[\frac{1}{r^{12}} - \frac{1}{r^6}\right]$ $\searrow$ const.

take $S = ar^n$ $\quad S' = anr^{n-1}$

$S'' = an(n-1)r^{n-2}$

$$\frac{1}{2\mu}an(n-1)r^{n-2} + \frac{1}{\mu}an r^{n-2} - \frac{1}{2\mu}a^2n^2r^{2n-2} + V(r)$$

$\frac{1}{2}n(n-1) + n = \frac{1}{2}n(n+1)$

$\downarrow$ = const

ϵr^{-12}

for LJ

$2n-2 = -12$

$2n = -10$

$n = -5$ ✓ $\quad S = ar^{-5}$!

$\frac{1}{2\mu}a^2 25 = \epsilon$

take $\mu = \frac{1}{2}$

$a = \frac{\sqrt{\epsilon}}{5}$!

$n-2 = -1$.

$\mu = 1$

$\frac{1}{2}a(n)(n+1)$ $\quad n = 1$!

$a = Z$ $\quad \underline{\underline{S = Zr}}$! Cusp-condition!

$$E_L = \frac{H\psi}{\psi} = \frac{He^{-S}}{e^{-S}}$$

$=$

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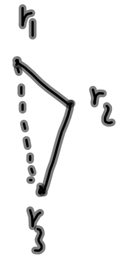
$$\Psi(r) = e^{-\sum_i s_1(r_i) - \sum_{i>j} \underbrace{s_2(r_{ij})}_{\text{two-particle}} - \sum_{i>j>k} s_3(r_{123})} \quad \text{Det}$$

$s_1(r_i) = Z r_i$



fermions.

Correlated basis function expansion.

↪ MC calculations.

only for Bosons

More probability theory: stochastic process

1) $P(x)$ pdd for X

2) $P_{XY}(x,y)$ joint pdd. for X + Y $\quad P(y) = \int dx\, P_{XY}(x,y)$

$P(x) = \int dy\, P_{XY}(x,y)$

3) $P_{XY}(x,y) = P_{X|Y}(x,y)P(y)$

↳ conditional prob. conditional on Y.

prob. on x, depending on Y.

4) $P_N(x_1 x_2 .. x_N) = P(x_N | x_{N-1} \cdots x_i ; x_{i-1} \cdots x_1)$

joint prob. for N particles

$P(x_{N-1} | x_{N-2} \cdots x_1)$

$P(x_{N-2} | \cdots)$

$P(x_2|x_1)P(x_1)$

Let $x_1, x_2 \cdots x_N$

be $X(\Delta t), X(2\Delta t) \cdots X(N\Delta t)$.

time-interpretation $\Rightarrow$ stochastic process

different types of

$X(t)$

$\parallel$

$P(x,t)$

$$P_N(x_1 \cdots x_N) = P_N(x_N) P_{N-1}(x_{N-1}) \cdots P_2(x_2) P_1(x_1)$$

total random process.

$$P_N(x_1 \cdots x_N) = P(x_N | x_{N-1}) P(x_{N-1} | x_{N-2}) \cdots P(x_3|x_2) P(x_2|x_1) P(x_1)$$

Markov process.

$$\langle f(\tilde{R})\rangle = I \pm \frac{\sigma_f}{\sqrt{n}} \qquad \sigma_f^2 = \langle f^2\rangle - \langle f\rangle^2$$

n = n-independent configuration

$$\frac{1}{10}\sum_{i=1} f(R_i)$$

$$\overbrace{R_0 \to R_1 \to R_2 \to R_3 \cdots \quad R_{10}} \cdots R_{20} \longrightarrow R_{30}$$

$R_1 \downarrow$ rejection $R_2 = R_1$

$R_2 \downarrow$ accept

↳ not entirely independent

block averaging

↓

10 - 100

Only Cartesian coordinates for many-particles.

$$|\tilde{\psi}(\tilde{R})|^2 dx_1 dy_1 dz_1 dx_2 dy_2 dz_2 \cdots$$

$$\cancel{|\psi(r)|^2 4\pi r^2 dr}$$

$$= |\psi(r)|^2 dx\,dy\,dz$$

$$r = \sqrt{x^2+y^2+z^2}$$

$$e^{-\frac{1}{2\Delta t}x^2} \qquad |\psi|^2 = e^{-2\alpha r^2} = e^{-2\alpha(x^2+y^2+z^2)}$$

$$2\alpha = \frac{1}{2\Delta t} \qquad \alpha \cdot$$

$$\Delta t = \frac{1}{4}\frac{1}{\alpha}$$

$$g \propto \sqrt{\Delta t}\, g_1$$

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Markov process :

$$P(x_N, x_{N-1}, \cdots x_2, x_1) = P(x_N, x_{N-1})\, P(x_{N-1}, x_{N-2}) \cdots P(x_2, x_1)\, P(x_1)$$

$$\underset{\text{final prob. dist}}{P(x_N)} = \int \underbrace{dx_{N-1} \cdots dx_1\; P(x_N, x_{N-1}) \cdots P(x_1)}_{\text{Path-integral}}$$

↳ in imaginary time.

$$= \int dx_{N-1}\, P(x_N, x_{N-1})\, P(x_{N-1})$$

$$P(x') = \int dx\, \underbrace{P(x', x)}_{\text{conditional prob.}}\, P(x) \qquad \vec{P}' = M \vec{P}$$

M

= prob. dist. for x', given x

$$\vec{P}_{N+1} = (M)^N \vec{P}_1$$

Choose $P(x', x)$ such that

$$P_N(x) \xrightarrow[N\to\infty]{} P_e(x)$$ ← equilibrium

$$\simeq |\psi|^2$$

How to choose $P_2(x',x)$ such that

$P_N(x) \to P_e(x)$ as $N \to \infty$

$1\,1 = \int dx'\, 1\, P(x',x)$

Requirement on $P(x',x)$:

i) $P(x',x) \geq 0$

ii) $\boxed{\int dx'\, P(x',x) = 1}$

1 is the left eigenvector of M with eigenvalue = 1

$$P_{n+1}(x') = \int dx\, P(x',x)\, P_n(x)$$

at equilibrium

Stationary condition

$$\boxed{P_e(x') = \int dx\, P(x',x)\, P_e(x)}$$

$P(x',x)$ $\neq$ symmetric

$$\vec{P}_e = M \vec{P}_e$$

$P_e(x)$ is the right eigenvector of M with eigenvalue = 1

In general

$$\int dx\, P(x',x)\, R_n(x) = \lambda_n R_n(x)$$

$$\int dx'\, L(x')\, P(x',x) = \lambda_n L_n(x)$$

$$P(x',x) = \sum_n \lambda_n L_n(x') R_n(x)$$

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All λ_n are < 1

"Proof" Let C be the max $|L_n(x)|$

$$\left| \int dx' \, L_n(x') \, P(x';x) \right| < C \underbrace{\left| \int dx' \, P(x';x) \right|}_{=1}$$

$$| \lambda_n L_n(x) | < C$$

$$|\lambda_n| < \frac{C}{|L_n(x)|} < 1$$

choose to be C

How to choose $p(x', x)$?

$$p(x', x) = w(x', x) + \underbrace{\left[1 - \int w(x', x)\, dx'\right]}_{\text{Prob. of NOT moving.}} \delta(x', x)$$

moving prob.

satisfy ii)

conditional prob.

$\int w(x', x)\, dx' < 1$

$$P_e(x') = \int p(x', x)\, P_e(x)\, dx$$

$$= P_e(x') + \int w(x', x) P_e(x)\, dx$$

$$- \int \underset{\substack{\shortparallel \\ dx}}{dx''}\, w(\underset{\substack{\uparrow \\ x}}{x''}, x')\, P_e(x')$$

$$P_e(x') = P_e(x') + \int dx \left[w(x' x) P_e(x) - w(x, x') P_e(x') \right]$$

choose $w(x', x)$ such that

$$\boxed{w(x', x) P_e(x) = w(x, x') P_e(x')}$$

detail-balance, condition

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Given $\underline{X}, \underline{Y}$ described by $P_{\underline{X}\underline{Y}}(x,y)$

what is $P_{\underline{Z}}(z)$ $\quad \underline{Z} = \underline{X} + \underline{Y}$? $\quad \hookrightarrow P_{\underline{X}}(x) P_{\underline{Y}}(y)$

$$P_{\underline{Z}}(z) = \int dx\, dy\, \delta(z-x-y)\, P_{\underline{X}\underline{Y}}(x,y)$$

$$= \int dx\, P_{\underline{X}\underline{Y}}(x, z-x)$$

$$P_{\underline{Z}}(z) = \int dx\, \underbrace{P_{\underline{X}}(x)\, P_{\underline{Y}}(z-x)}_{\text{convolution}}$$

Let $\underline{Y} = \Delta\underline{X}$

$$\underline{Z} = \underline{X} + \Delta\underline{X}$$

$$P_1(x') = \int dx\, P_1(x)\, P_2(x', x)$$

$\hookrightarrow P(x'-x) \quad = \Delta x$

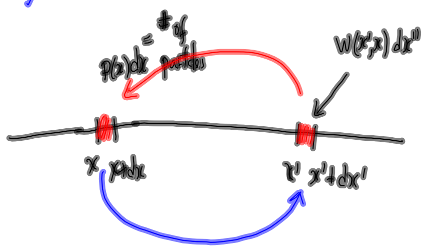
$$\underline{X}' = \underline{X} + \Delta\underline{X}$$ given by $P_2(\Delta x)$

Detail-balance condition:

$$W(x',x)P_e(x) = W(x,x')P_e(x')$$

at equilibrium

once in equilibrium, stay in equilibrium.



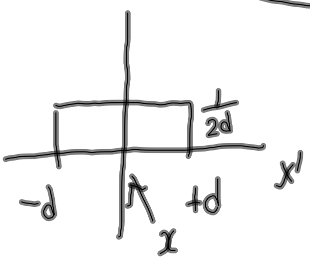
to devise a $W(x',x)$

$$W(x',x) = T(x',x)\,A(x',x)$$

T: trial move prob. A: acceptance prob.

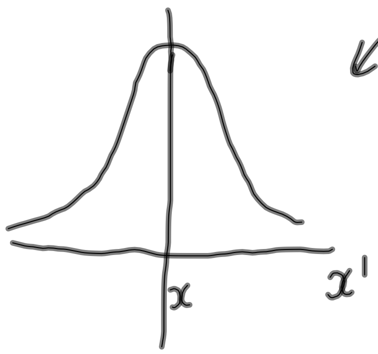
take $T(x',x)$ to be symmetric

$$T(x',x) = \frac{1}{2d} \quad \text{if } |x'-x|<d$$
$$= 0 \quad |x'-x|>d$$



$$x' = x + d*(2*\text{ran} - 1)$$

or $$T(x',x) = \frac{1}{\sqrt{2\pi\delta t}}\, e^{-\frac{1}{2\delta t}(x'-x)^2}$$



$$x' = x + \sqrt{\delta t}\, g$$

g: Gaussian r.v.

$$W(x',x)P_e(x) = W(x,x')P_e(x')$$

$$\overset{\shortparallel}{\cancel{T(x',x)}}A(x',x)P_e(x) = \cancel{T(x,x')}A(x,x')P_e(x')$$

Let $P_e(x) = e^{-S(x)}$

$$A(x',x)e^{-S(x)} = A(x,x')e^{-S(x')}$$

$$A(x',x) = A(x,x')e^{-\Delta S} \qquad \Delta S = S(x')-S(x)$$

choose $A(x',x)$ to be a function just of $\Delta S(x',x)$

$$A(\Delta S) = A(-\Delta S)e^{-\Delta S}$$

$$A(\Delta S)e^{\frac{1}{2}\Delta S} = A(-\Delta S)e^{-\frac{1}{2}\Delta S}$$

$\overset{\shortparallel}{F(\Delta S)}$ is an Even function of ΔS!

$$A(\Delta S) = F(\Delta S)e^{-\frac{1}{2}\Delta S}$$

$$= e^{-\frac{1}{2}|\Delta S|}e^{-\frac{1}{2}\Delta S}$$

if $\Delta S < 0$

max $A = 1$

then if $\Delta S > 0$

$$= e^{-\Delta S} = \frac{P_e(x')}{P_e(x)}$$

$$A(\Delta S) = \begin{cases} 1 & \text{if } \Delta S < 0 \\ e^{-\Delta S} & \text{if } \Delta S > 0 \end{cases}$$

$$= \min(1, e^{-\Delta S})$$

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Generalization of Metropolis

Let now take $T(x',x)$ NOT symmetric

$$T(x',x) = \frac{1}{\sqrt{2\pi\Delta t}} e^{-\frac{1}{2\Delta t}\left(x'-x-v(x)\Delta t\right)^2}$$

with a drift velocity field.

$$x' = x - v(x)\Delta t + \sqrt{\Delta t}\, g$$

$$T(x',x)A(x',x) = T(x,x')A(x,x')e^{-\Delta S}$$

Langevin algorithm

$$A(x',x) = A(x,x')\frac{T(x,x')}{T(x',x)}e^{-\Delta S}$$

$$= A(x,x')\, e^{-\Delta\tilde{S}} \qquad e^{-\Delta\tilde{S}} = \frac{T(x,x')}{T(x',x)}e^{-\Delta S}$$

$$A(\Delta\tilde{S}) = \min\left(1, e^{-\Delta\tilde{S}}\right)$$

$$= \min\left(1, \underbrace{\frac{T(x,x')P_e(x')}{T(x',x)P_e(x)}}_{=R}\right)$$

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Monte Carlo $\rightarrow$ sampling $P_e(x) = P_e(\vec{R})$

1) Inversion in 1D

2) Metropolis in the general case : $\vec{R}$

3) Langevin algorithm :

Consider the diffusion equation (imaginary time Schrodinger Eq.)

$$-\frac{\partial\psi}{\partial t} = -\frac{1}{2}\nabla^2\psi$$

$$\psi(x', t+\delta t) = \int G(x', x, \delta t)\,\psi(x, t)\,dx$$

$$G(x', x; \delta t) = \frac{1}{\sqrt{2\pi\delta t}}\,e^{-\frac{1}{2\delta t}(x'-x)^2}$$

$$\vec{X}' = \vec{X} + \sqrt{\delta t}\,\vec{g}$$

if each particle undergoes Gaussian random walk their density

as $t \rightarrow \infty$

uniform equilibrium distribution

To get at a non-trivial $\rho_e(x)$,

$$\rho(x,t) = \underbrace{\phi(x)}_{\text{distribution we wanted}}\underbrace{\psi(x,t)}_{\to\ \text{const}} \qquad -\frac{\partial}{\partial t}\psi = -\frac{1}{2}\nabla^2\psi$$

$$\rho(x,t) \xrightarrow[t\to\infty]{} \text{const}\ \phi(x)$$

$$-\frac{\partial\rho}{\partial t} = \phi\left(-\frac{\partial\psi}{\partial t}\right) = -\frac{1}{2}(\nabla^2\psi)\phi$$

express in terms of ρ

$$\phi\nabla^2\psi = \vec\nabla(\phi\vec\nabla\psi) - \underbrace{\vec\nabla\phi\,\vec\nabla\psi}_{-\nabla(\psi\nabla\phi) + \psi\nabla^2\phi}$$

$$= \vec\nabla(\phi\vec\nabla\psi - \psi\nabla\phi) + \underbrace{\phi\psi}_{\rho}\left(\frac{\nabla^2\phi}{\phi}\right)$$

$$= \vec\nabla\big(\nabla(\phi\psi) - 2\psi\nabla\phi\big)$$

$$= \vec\nabla^2\rho - 2\vec\nabla\left(\rho\,\frac{\nabla\phi}{\phi}\right) + \rho\left(\frac{\nabla^2\phi}{\phi}\right)$$

$$\boxed{-\frac{\partial\rho}{\partial t} = -\frac{1}{2}\nabla^2\rho + \vec\nabla\left(\rho\,\frac{\vec\nabla\phi}{\phi}\right)} + \left(\frac{-\frac{1}{2}\nabla^2\phi}{\cancel{\phi}}\right)\rho$$

We $\quad -\frac{\partial\rho}{\partial t} = -\frac{1}{2}\nabla^2\rho \quad$ diffusion

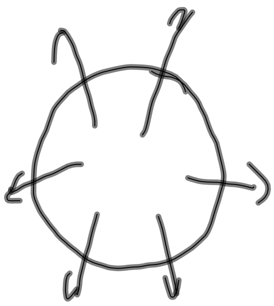
$$\vec v = \frac{\vec\nabla\phi}{\phi}$$

$$-\frac{\partial\rho}{\partial t} = \vec\nabla\cdot(\rho\vec v)$$

equation of continuity

$J = \rho\vec v$

current density



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$$\boxed{-\frac{\partial}{\partial t}\rho = -\frac{1}{2}\nabla^2\rho + \vec{\nabla}(\rho\vec{v})}$$

Fokker-Planck equation.

$$0 = \vec{\nabla}\left(-\frac{1}{2}\vec{\nabla}\rho + \rho\vec{v}\right)$$

$$\frac{\vec{\nabla}\rho_e}{\rho_e} = 2\vec{v} = 2\frac{\vec{\nabla}\phi}{\phi}$$

$$\rho(x,t) \xrightarrow[t\to\infty]{} \rho_e = \phi^2$$

Can simulate

$$x' = x + \sqrt{\Delta t}\, g$$

$$-\frac{\partial\rho}{\partial t} = \vec{\nabla}(\rho\vec{v})$$

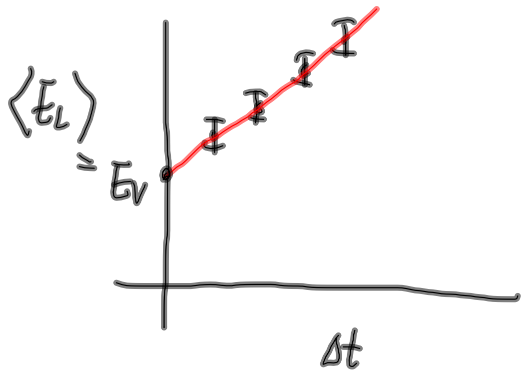
$$\frac{dx}{dt} = v(x)$$

$$x' = x + v(x)\Delta t$$

$$\vec{v} = \frac{\vec{\nabla}\phi}{\phi}$$

$$x' = x + v(x)\Delta t + \sqrt{\Delta t}\, g$$

first order Langevin algorithm.



if $\phi = e^{-\alpha r}$

$$\vec{v} = \frac{\nabla\phi}{\phi} = -\alpha\hat{r}\frac{\cancel{\phi}}{\cancel{\phi}}$$

$$\boxed{\vec{v} = -\alpha\hat{r}}$$